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Structural, optical, photoluminescence and photocatalytic characteristics of sol-gel derived CeO_2-TiO_2 films

Amita Verma* & Amish G Joshi

Electronic Materials Division, National Physical Laboratory, New Delhi 110 012, India
Email: amitaverma75@gmail.com

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CeO_2-TiO_2 films with different Ce/Ti mole ratios have been obtained using a simple sol-gel process. The films (1:0.25 and 1:0.5) containing more than 50% CeO_2 content show nanocrystalline characteristics. X-ray photoelectron spectroscopic study shows the variation of Ce^{4+}/Ce^{3+} ratio with increasing TiO_2 content. Films with greater CeO_2 content exhibit higher porosity. The observed photoluminescence in the films is attributed to various defects resulting from crystallization and also to the relative amount of Ce^{3+} in the mixed oxide matrix. The transparency in the films appears to be inversely related to their photoluminescence activity, since the 1:0.5 film, which exhibits the best photoluminescence response, is incidentally also the least transparent film. The presence of photocatalytic activity in these films shows their potential use as an efficient photocatalyst.

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Photocatalytic reactions sensitized by TiO_2 and other semiconducting materials have attracted extensive interest for their potential for solving energy and environmental issues. Several cerium titanates have been investigated for their photocatalytic activity. Mixed CeO_2-TiO_2 films are reported to decolorize methyl orange solutions upon irradiation of the UV light[1]. Luminescent properties of the rare earth oxides and other semiconductor and insulator oxides are widely used to study the active doping sites. Medical diagnostics, high-density optical storage, opto-electronic devices and flat panel displays are some of the major examples of the utility of these materials[2]. The width and the relative intensity of luminescent emission bands are frequently affected by the nature of the lattice. This feature can be used to tune the emission of the materials depending on the practical applications. Thus, characteristics of rare earths luminescence in different compositions are of importance. Though there are some reports on bulk powders, only a few reports deal with rare earths oxides as thin films, which are of great importance for technological applications such as light emitting devices and flat panel displays[3-6]. Sol-gel technology allows the architectural design of coatings and multilayered thin films in several types of geometries[7-12]. This method can be used for fabrication of thin films of controlled thickness with the additional advantage of the possibility to dope them with a large variety of organic and inorganic compounds.

In the present study, CeO_2-TiO_2 films have been obtained using a simple sol-gel process. The structural, morphological, photoluminescence (PL) and photocatalytic characteristics of films with different Ce/Ti mole ratio have been investigated.

Materials and Methods

Preparation of deposition solutions and films

To 2.5 g of $CeCl_3.7H_2O$ (Merck) dissolved in 30 ml of C_2H_5OH (Merck), 1.907g of titanium propoxide (Aldrich) was added to obtain a deposition solution containing Ce/Ti mole ratio of 1:1. Apart from this composition, other mole ratios such as 1:0.25, 1:0.5 and 1:3 were also studied. These deposition solutions were stored at room temperature in closed glass vessels to prevent rapid precipitation of the alkoxide due to hydrolysis. During the experimental process, the room temperature was kept at 20±5°C and the humidity was maintained at 60±10 %. Addition of alkoxide to the ethanolic solution of the cerium salt induced a color change so that the color of the deposition solutions was bright yellow. The intensity of the yellow color was observed to increase with increasing proportion of titanium propoxide. The gelation period of the sol decreased with the increased

proportion of titanium propoxide, and showed a strong dependence upon the ambient temperature and humidity.

Micro slide glass substrates were spin coated at 3000 rpm for 35 s by the freshly prepared deposition solutions to achieve the as-deposited mixed CeO_2-TiO_2 films. The as-deposited films thus obtained were dried at room temperature for 15 min., and subsequently densified for 5 min. in air at 500°C. Pale yellow homogeneous films with high adherence to the substrates and excellent chemical as well as mechanical stability were finally obtained.

Characterization of films

X-ray diffraction (XRD) patterns of the films were recorded in the 2θ range from 5° to 70° at an incidence angle of 1° with a D8 Advanced Bruker diffractometer. Fourier transform infrared (FTIR) spectra of the films in the reflection mode were recorded in the wavenumber range of 400-4000 cm^{-1} on a Perkin-Elmer (model BX2) spectrophotometer. The X-ray photoelectron spectroscopic (XPS) data were obtained on a Perkin-Elmer (P4I, model 1257) instrument. The surface morphology of the films was observed by scanning electron microscopy (SEM) on a JEOL JSM 840 scanning electron microscope. Optical transmittance and reflectance data of the films were measured in the range of 300-2000 nm using a UV 3101 PC Shimadzu spectrophotometer. The photocatalytic activity of the samples was evaluated by eosin (yellow) decomposition under UV-visible light irradiation. The irradiation was provided by 80 W mercury vapor light centered at 365 nm wavelength. The initial concentration of eosin (yellow) in water was fixed at 4×10^{-5} *M*. The extent of eosin decomposition was determined by measuring its absorbance at different time periods. Photoluminescence (PL) measurements were carried out at room temperature in the 300-700 nm range using a Perkin-Elmer LS055 spectrometer at an excitation wavelength of 240 nm.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the CeO_2-TiO_2 films. It is evident from the figure that crystallization of CeO_2 has taken place in the 1:0.25 and 1:0.5 compositions along the (111) crystallographic plane only. The 1:1 and 1:3 compositions, however, exhibit amorphicity to X-rays. The CeO_2 crystallite size for the 1:0.25 and 1:0.5 films as found using the Debye Scherer formula is 16 nm. Another important observation in the 1:0.5 composition is the crystallization of the mixed compound, $CeO_{1.6}.2TiO_2$. Importantly, the diffraction peaks in these films are weak in intensity due to their small nano-range crystallite size. However, the *d*-values of CeO_2 and $CeO_{1.6}.2TiO_2$ crystalline phases

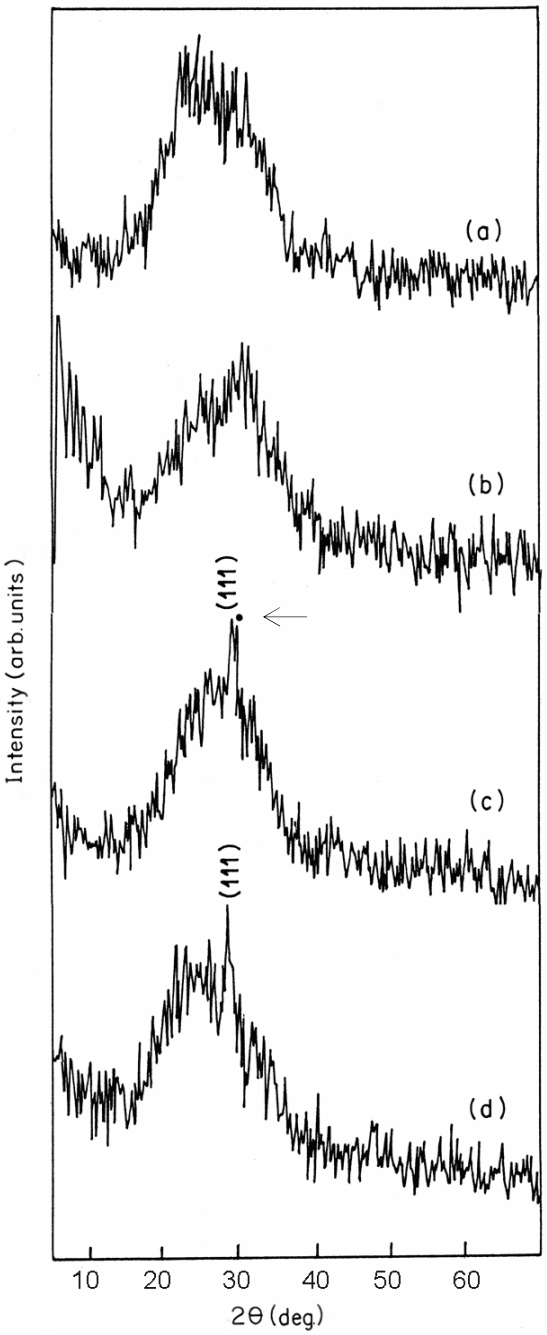

Fig. 1— X-ray diffraction patterns of films with different Ce/Ti mole ratios thermally treated at 500°C for 5 min. [(a) 1:3; (b) 1:1; (c) 1:0.5; (d) 1:0.25. Symbol "•" denotes the diffraction peak of $CeO_{1.6}.2TiO_2$].

in the present work match very well with the *d*-values of CeO_2 and $CeO_{1.6}.2TiO_2$ phases reported in the literature[13]. Furthermore, as is shown later in this study, the 1:0.5 composition demonstrates the highest PL activity. The existence of the mixed compound in 1:0.5 ratio is primarily responsible for this result. The absence of mixed compound in the 1:0.25 film seems to be the reason for its lower PL activity in comparison to that of the 1:0.5 film. The amorphous characteristics in 1:1 and 1:3 compositions have led to their lower PL response.

The elucidation of structural features using the FTIR study shows the formation of TiO_2 network in all the films. The films exhibit bands assigned to ν(Ti-O-Ti) and ν(Ti-O) near 544 and 798 cm^{-1} (longitudinal optical mode) respectively[14]. The red frequency shift of the LO mode of amorphous TiO_2 from ~ 870 cm^{-1} to ~ 798 cm^{-1} is a consequence of the presence of CeO_2 nanograins. The intensity of the band, which is assigned to longitudinal optical (LO) mode of amorphous TiO_2 phase, shows an increase with the increase in TiO_2 content in the films. This increased band intensity is also attributable to the higher thickness of these films. The degree of contribution from the ν(Ti-O-Ti) and ν(Ti-O) stretching vibrational modes varies for these films depending on their TiO_2 content. Importantly, the 1:0.25, 1:0.5, and 1:1 compositions exhibit relatively higher intensity of the band assigned to the ν(Ti-O-Ti) mode. The 1:3 composition, however, shows a reverse trend and demonstrates more intensity for the band assigned to ν(Ti-O) vibrational mode. This indicates that due to the higher proportion of Ti in the 1:3 composition, the TiO_2 network formed in this film is stronger. It also suggests that the conversion of Ti-O-Ti polymeric chains with different lengths to the oxide network is nearly complete in the 1:3 film.

X-ray photoelectron spectroscopic studies

The deconvoluted XPS core-level spectra of Ce in the binding energy range of 870-930 eV are shown in Fig. 2. The films show spin-orbit splitting of the Ce 3*d* level, manifested as Ce3$d_{5/2}$ and Ce3$d_{3/2}$. Deconvolution of the peaks into ten components has been carried out. These films show the presence of Ce in both Ce^{4+} [882.7 eV (v), 888.2 eV (v´´), 899.2 eV (v´´´), 901 eV (u), 907.6 eV (u´´), 916.7 eV (u´´´)] and Ce^{3+} [882 eV (v_o), 886.2 eV (v´), 903.05 eV (u_o), 905 eV (u´)] states. The compositions containing higher ratio of Ce are observed to possess greater proportion of Ce^{4+} state. With increasing Ti content in the samples, a small peak corresponding to the 3+ state of Ce appears at 886.2 and 903.05 eV for 3$d_{5/2}$ and 3$d_{3/2}$ spin-orbit states, respectively. This peak grows gradually with increasing Ti content suggesting thereby the $Ce^{4+} \rightarrow Ce^{3+}$ conversion. The reduction of Ce^{4+}/Ce^{3+} ratio with increased Ti content in the films suggests the influence of Ti in facilitating Ce^{4+} reduction. Earlier, XPS studies by Trinchi *et al.*[15] have also shown an increase in the Ce^{3+} content for

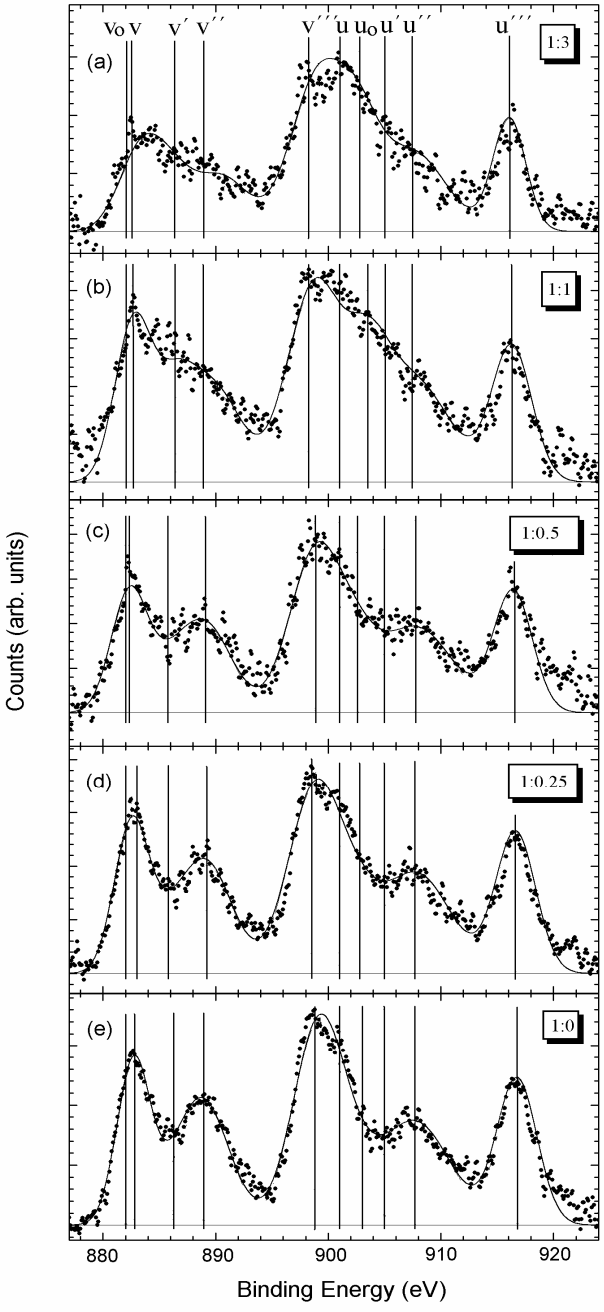

Fig. 2— Normalized Ce core-level spectra of films with different Ce/Ti mole ratios. [(a) 1:3; (b) 1:1; (c) 1:0.5; (d) 1:0.25; (e) 1:0].